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Association of Hydrocarbon Hydroperoxides

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The results of studies on the association of hydrocarbon hydroperoxides and the formation of their complexes with alcohols and aromatic, dienic, and olefinic hydrocarbons are reviewed. The role of the intermolecular hydrogen bond in the decomposition of hydrocarbon hydroperoxides is demonstrated.
The bibliography includes 53 references.

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1. INTRODUCTION

The oxidation of hydrocarbons by molecular oxygen (autoxidation) constitutes an important method for the industrial preparation of valuable oxygen-containing compounds. Numerous studies on the liquid-phase oxidation of various hydrocarbons have now firmly established that hydroperoxides are the first stable products of their oxidation[1-5]. The molecules of organic substances with a hydroxy-group (alcohols, phenols, hydroperoxides, etc.) are known[6,7] to be capable of associating with one another and with the molecules of other compounds by hydrogen bonding, the presence of which has a significant effect on the reaction kinetics. The study of the association processes of hydroperoxides and their derivatives makes it possible to assess more fully the results obtained in the liquid-phase oxidation of hydrocarbons and also to suggest radical improvements to the process. Hydroperoxides play a fundamental role in polymer oxidation and degradation processes, promoting chain branching. A very important factor here is that the branching efficiency, i.e. the decomposition rate constants and the number of radicals formed per decomposition step, depends on the physicochemical state of the hydroperoxide. The association equilibrium constants enter into all the kinetic equations and therefore the knowledge of these constants and of the coordination numbers is always essential. In the present paper an attempt is made to review data obtained in the study of the association of hydrocarbon hydroperoxides by ^{1}H NMR and infrared spectroscopy.

2. SELF ASSOCIATION OF HYDROCARBON HYDROPEROXIDES

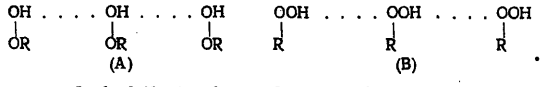
Up to 1950 only the infrared spectra of hydrogen and deuterium peroxides were investigated, the 870 cm^{-1} band being attributed to the O — O bond[8].

The infrared spectra of isopropylphenyl, tetralyl, cyclohexyl, and t-butyl hydroperoxides were recorded in 1951. Sherve et al.[9] attribute three frequencies to the vibrations of the C — O — O — H group: 840, 880 (OOH), and 3600 cm^{-1} ($OH_{stretch}$). The shift of the absorption maximum towards shorter wavelengths on dilution with carbon disulphide indicates the presence of hydrogen bonds in the system. Karyakin et al.[10] established that the vibrations of the hydroperoxy-group C — O — O — H are fairly active in the infrared and have the following characteristic frequencies (mean values):

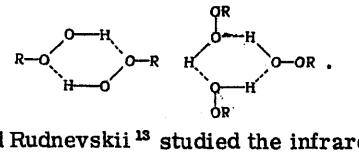
C—O—O—H_{def}	840	cm^{-1}
O—$O_{stretch}$	880	»
C—$O_{stretch}$	1151	»
O—H_{def}	1300	»
O—$H_{stretch}$	3450	»
First overtone	6800	» .

The presence of these frequencies in the infrared spectrum of any compound (primarily two of them: 840 and 3450 cm^{-1}) may serve as an indication that the given compound is a hydroperoxide.

Table 1 lists the vibration frequencies of the C — O — O — H group in various hydroperoxides. A number of studies have been made on the structure of hydroperoxide association complexes. Thus Minkoff[11] suggested on the basis of the stretching vibration frequencies of the OOH group that there are two types of association (A and B) in hydroperoxides (3.01 and 2.92 μm bands):



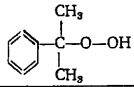
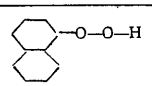
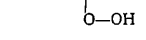
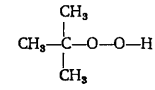
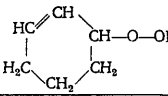
It was concluded that, depending on the nature of the monomer (free hydroperoxide molecules) and the concentration of the hydroperoxide in heptane solution, the isomers of the hydroperoxide exist in dimeric and trimeric forms[12]:



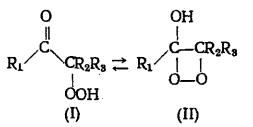
Zharkov and Rudnevskii[13] studied the infrared spectra of t-butyl hydroperoxide solutions in carbon tetrachloride in the range 3200 — 3600 cm^{-1}. They were the first to calculate for hydrocarbon hydroperoxides two association constants from the change in the intensity of the absorption band due to the OH group at 3540 cm^{-1}: the dimerisation constant and the constant for a higher degree of association, together with the dimerisation energy (6.3 ± 1.0 kcal $mole^{-1}$) and the energy of further association (2.8 ± 0.7 kcal $mole^{-1}$). The authors put forward a mechanism for the association of t-butyl hydroperoxide which includes the formation of a cyclic dimer via two hydrogen bonds

with subsequent linear association which probably takes place via the oxygen atoms of the hydroperoxy-groups in the cyclic dimer not involved in hydrogen bonding.

Table 1. C—O—O—H vibration frequencies in the infrared spectra of various hydroperoxides[10].

Hydroperoxide	Structural formula	Wave number, cm^{-1}					
		C—O—O—H def.	O—O stretch	C—O stretch.	O—H def.	O—H stretch	O—H first overtone
Isopropylphenyl hydroperoxide		837	881	1155	1325	3450	6740
Tetralyl hydroperoxide		833	885	1150	1300	3380	6840
Decalyl hydroperoxide		837	873	1155	1310	3400	6900
Hydroxymethyl hydroperoxide		840	880	no data	no data	3400	6800 6450
Heptyl hydroperoxide		862		1135	1300	3450	no data
t-Butyl hydroperoxide		846	888	1194	1365	3520	ditto
Cyclohexenyl hydroperoxide		838	856	1160	1305	3450	»
Hydrogen peroxide	H—O—O—H		870	—	1370	3417	»

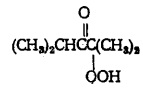
In recent years the proton magnetic resonance method (^{1}H NMR) has been widely used in the study of hydrogen bonds[14-20]. The ^{1}H NMR chemical shifts of a number of alkyl hydroperoxides were first measured by Japanese investigators[7]. The proton resonance in the OOH group occurs at a lower field than the proton resonance in the CH_3 group approximately by 9.06 p.p.m. (at a working frequency of 27 030 MHz and H_0 = 6300 G). The signal of the hydroperoxy-proton is close to that of the carboxy-group in aliphatic acids (9.9 — 10.3 p.p.m.), occurring in a lower field than the OH proton signal in alcohols (3.7 — 4.44 p.p.m.). The shift of the signal due to the OOH proton as a function of concentration is attributed to the formation of a hydrogen bond. Richardson and Steed[18] studied the structure of α-ketohydroperoxides and also the intermolecular and intramolecular hydrogen bonds in these compounds. They established that the equilibrium in reaction (1) is fully displaced to the left:



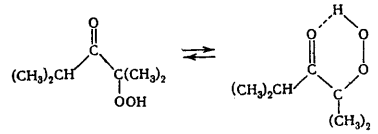
(1)

(I) (II)

The proton magnetic resonance spectrum of the compound

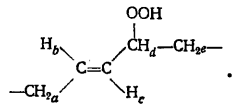


shows that the proton linked to oxygen gives rise to a signal at low field (9.39 p.p.m. for an 11% solution in carbon tetrachloride), characteristic of the hydroperoxy-group. This finding led to the conclusion that the compound is most likely to exist in the hydroperoxy-form (I) [Eqn. (1)]. On the basis of the infrared spectra, the authors calculated the enthalpy (−1.45 kcal mole^{-1}), free energy (−0.12 kcal mole^{-1}), and entropy (−4.3 e.u.) of the monomer — dimer equilibrium for form (I). The low enthalpy for form (I) can be explained by the formation of a strong intermolecular hydrogen bond according to the following scheme:



(2)

According to the infrared spectroscopic data, the energy of this bond is −1.86 kcal mole^{-1}. In the ^{1}H NMR spectra of the monohydroperoxides of oleic and linoleic acid esters[19], the hydroperoxy-group gives rise to a broad signal at 8.92 p.p.m. (30 — 40% solution in carbon tetrachloride) and the infrared spectrum shows a band due to the vibrations of the OH group at 3440 cm^{-1}. These hydroperoxides probably have the following structure:



The chemical shifts of the individual groups of protons and the spin — spin coupling constants are listed below:

δ_a, p.p.m.	δ_b, p.p.m.	δ_c, p.p.m.	δ_d, p.p.m.	δ_e, p.p.m.	J_{ab}, Hz	J_{bc}, Hz	J_{cd}, Hz	J_{ac}, Hz	J_{bd}, Hz
2.10	5.60	5.30	4.11	1.44	±6.25	±15.59	±8.04	±0.96	±1.17

The splitting constant (15.6 Hz) confirms that the (*b*) and (*c*) protons are in the *trans*-position. In the spectrum of 1-tetralyl hydroperoxide the signal due to the hydroperoxy-proton is at 8.65 p.p.m., while in the spectrum of the monohydroperoxide of methyl-linoleic acid prepared in different ways the signal is at 9.0 and 8.8 p.p.m. Kucher et al.[20] studied the dependence of the chemical shifts of the proton in the OOH group of isopropylphenyl hydroperoxide on its concentration in various solvents: carbon tetrachloride, isopropylbenzene, and nitrobenzene. Extrapolation of the concentration curve (in carbon tetrachloride) to infinite dilution yields the chemical shift δ = 6.55 p.p.m., while in the pure hydroperoxide δ = 8.62 p.p.m. The authors estimated the dimer ⇌ monomer equilibrium constants from the slope of the $\delta = f(c)$ concentration curve at infinite dilution and obtained a value of 19.5.

The self-association processes of isopropylphenyl, t-butyl, and t-pentyl hydroperoxides have been analysed on the basis of ^{1}H NMR data[21-23].

The thermodynamic parameters of the hydrogen bonds have been calculated from the temperature and concentration variation of the chemical shift of the proton in the

OOH group of hydroperoxides in an inert solvent (Table 2). It has been shown (see also Zharkov and Rudnevskii[13]) that the self-association of hydroperoxides takes place via the formation of cyclic dimers with subsequent linear association of the dimer with hydroperoxide molecules. The calculated enthalpies of formation of the hydrogen bond in hydroperoxides makes it possible to compare them in terms of the strength of the hydrogen bond with other classes of compounds and to devise a general mechanism of the self-association of hydroperoxide molecules. The hydrogen bond in hydroperoxides is weaker than in other compounds containing hydroxy-groups (alcohols, phenols, and acids).

Table 2. Thermodynamic parameters for the formation of hydrogen bonds by hydroperoxides[21,22].

Hydroperoxide	K_{dim} at 21°C (p.p.m.)$^{-1}$	$K_{subs.\ assn.}$ at 21°C, (p.p.m.)$^{-1}$	$-\Delta H_{dim}$, kcal mole^{-1}	$\Delta H_{subs.\ assn.}$ kcal mole^{-1}	$-\Delta S_{dim}$, cal mole^{-1} deg^{-1}	$-\Delta S_{subs.\ assn.}$, cal mole^{-1} deg^{-1}
t-Butyl hydroperoxide	19±2	180±20	6.6±1	3±1	17±2	0±3
t-Pentyl hydroperoxide	18±2	180±15	6.5±1	3±1	17±2	0±2
Isopropylphenyl hydroperoxide	15±2	146±15	7.7±1	2.2±1	21±3	2±3

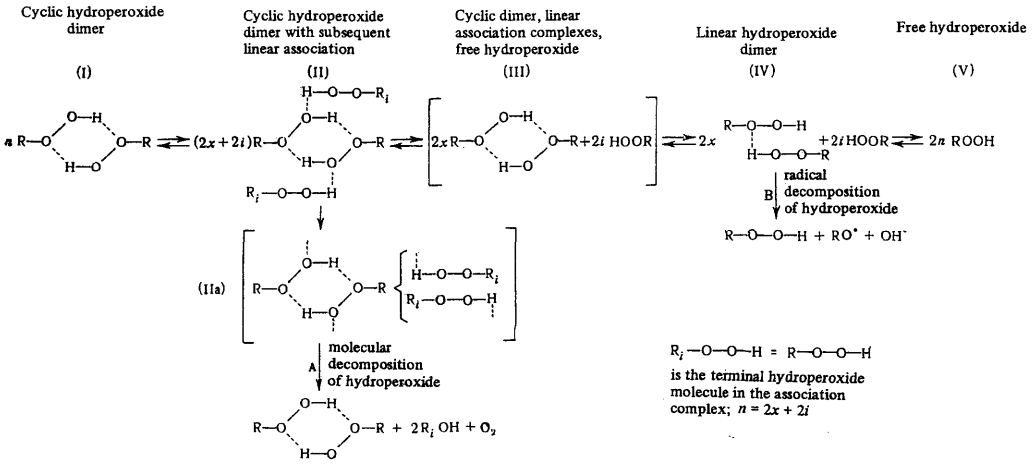
The mechanism of the self-association of hydroperoxide molecules devised by the authors is given below[23]. Generally speaking, one can suggest that at comparatively low temperatures the hydroperoxide exists in forms (I) — (V). However, examination of the relative equilibrium constants K_{12} for the monomer ⇌ cyclic dimer equilibrium [forms (V) and (I)] and the equilibrium constants for the subsequent linear association [forms (I) and (II)] at different temperatures showed that, with decrease of temperature, K_{12} increases faster than does $\overline{K}$.[21,22] One should then expect that under certain conditions the constants will become equal (for example, near −40°C for isopropylphenyl hydroperoxide) and that at lower temperatures dimerisation will predominate [form (I)].[23]

With increase of temperature, one of the dimers of form (I) decomposes with formation of form (II). It was found that the enthalpy of formation of the overall hydrogen bond in the cyclic dimer is 6 — 8 kcal mole^{-1}, while that for the hydrogen bond formed in subsequent association is only 2 — 3 kcal mole^{-1}. In its turn form (II) can dissociate into a cyclic dimer and the linear association complex [forms (III) and (IV)]. The cyclic dimer decomposes further into form (IV) and then into form (V).

The formation of a hydrogen bond is known[24] to weaken the H — O and O — O covalent bonds in the molecule of the proton donor and to strengthen the bonds adjoining the oxygen atom in the acceptor molecule. Thus in the hydroperoxide molecule, which is a donor in form (IV), the weakest O — O bond is weakened further by the formation of an intermolecular hydrogen bond. This leads to a cleavage of only one hydroperoxide molecule in form (IV) via the familiar mechanism (see the above mechanism, reaction B) of the unimolecular decomposition of the hydroperoxide with formation of free radicals.

In the association complex comprising the cyclic hydroperoxide dimer with subsequent linear associations [form (II)], the terminal hydroperoxide molecules may be in the immediate vicinity of one another owing to their polar interaction. Moreover, in these molecules, as in form (IV), the O — O bonds are weakened. All these factors suggest that both hydroperoxide molecules decompose simultaneously without the formation of free radicals (reaction A), in agreement with the usually observed second order of the thermal decomposition reaction of hydroperoxides[26]. The second order decomposition reaction of hydroperoxides is observed at high hydroperoxide concentrations, i.e. when association complexes of type (II) predominate in solution. The main products of reaction A are an alcohol and molecular oxygen. The only products of the thermal decomposition of t-butyl hydroperoxide (95 — 100°C) are trimethylmethanol and oxygen[27]. Dimethylphenylmethanol and oxygen were also found in the products of the thermal decomposition of isopropylphenyl hydroperoxide[28].

The mechanisms of the unimolecular and bimolecular thermal decomposition of hydroperoxides discussed above lead to the conclusion that the hydroperoxide molecules, which behave as proton acceptors in forms (II) and (IV),



Mechanism of the self association and the uni- and the bi-molecular decomposition of hydrocarbon hydroperoxides in inert solvents.

function as reaction catalysts ("autocatalysis"). In the cyclic dimer the hydrogen bonds are stabilised in the six-membered ring where the covalent bonds are not weakened, since the effects of the hydrogen bonds cancel out. This leads to the conclusion that the cyclic hydroperoxide dimer is the most stable association complex from the standpoint of the thermal stability of hydroperoxides. The thermal stability of the hydroperoxide in form (I) is close to that of the free hydroperoxide [form (V)].

The relative stabilities of the cyclic dimers of various hydrocarbon hydroperoxides are determined by the energy of the hydrogen bonds in the hydroperoxide molecules involved in their formation. The higher the hydrogen bond energy, the more stable the ring. Thus the equilibrium between forms (I) and (IV) of the hydroperoxides forming stable rings is displaced to the left and in this case the probability of the formation of form (IV) is lower than for hydroperoxides forming less stable rings.

On this hypothesis, isopropylphenyl hydroperoxide (ΔH = 7.7 kcal mole^{-1}) should have a higher thermal stability than t-butyl hydroperoxide (ΔH_{12} = 6.6 kcal mole^{-1}) and t-pentyl hydroperoxide (ΔH_{12} = 6.5 kcal mole^{-1}). On the other hand, the higher the hydrogen bond strength in linear association complexes of form (II) ($\Delta\bar{H}$ = 3.0 kcal mole^{-1} for t-pentyl and t-butyl hydroperoxides and $\Delta\bar{H}$ = 2.2 kcal mole^{-1} for isopropylphenyl hydroperoxide), the greater the shift, other conditions being equal, of the equilibrium between forms (II) and (III) towards form (II), in which two $R_i-O-O-H$ molecules are in a position energetically favourable for decomposition and where in addition the O — O bonds are weakened owing to the stronger hydrogen bond.

From this standpoint, isopropylphenyl hydroperoxide should also have a higher thermal stability than t-pentyl and t-butyl hydroperoxides.

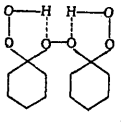
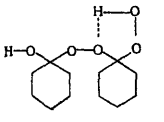
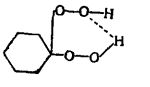
Conclusions concerning the different thermal stabilities of hydroperoxides based on the properties of the hydrogen bond are consistent with thermal stability data. Thus pure isopropylphenyl hydroperoxide is stable in saturated hydrocarbon solutions at 130 — 140°C,[28] while t-butyl hydroperoxide is cleaved at an appreciable rate at a temperature as low as 90°C.[29] It is also known[30] that t-pentyl hydroperoxide decomposes in octane at 110°C.

3. INTRAMOLECULAR HYDROGEN BONDS IN HYDROPEROXIDES

Hydroperoxides can form intramolecular hydrogen bonds in addition to addition to intermolecular complexes. The intramolecular hydrogen bond in isopropylphenyl hydroperoxide between the OOH group and the π electrons of the aromatic ring has been investigated by infrared spectroscopy[31]. In the infrared spectrum the OH absorption band consists of a doublet with maxima at 3497 and 3530 cm^{-1}. The 3530 cm^{-1} band was assigned to the vibrations of the free OH group and the 3497 cm^{-1} band to the vibrations of the bound OH group. The authors calculated from the temperature variation of the intensities of these bands that the energy of the intramolecular hydrogen bond was 0.9 ± 0.10 kcal mole^{-1}. The presence of an intramolecular hydrogen bond between the OOH group in isopropylphenyl hydroperoxide and the aromatic π electrons was confirmed[32].

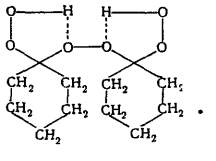
Terent'ev and Antanovskii studied the intramolecular hydrogen bonds in a number of hydroperoxides[33,34]. Table 3 lists the shifts $\Delta\nu$ of the band due to the C — O — O — H group on formation of an intramolecular hydrogen bond and the bond energies E_H. The authors calculated E_H for di-(1-hydroperoxycyclohexyl) peroxide from the intensity of the single absorption band at 3435 cm^{-1}, characteristic of its C — O — O — H group.

Table 3. The shifts $\Delta\nu$ of the bands due to the C — O — O — H group on formation of an intramolecular hydrogen bond and the intramolecular hydrogen bond energies[34] E_H.

Hydroperoxide	$\Delta\nu$, cm^{-1}	E_H, kcal mole^{-1}
Isopropylphenyl hydroperoxide	33 28	0.9±0.1[31]
Tetralyl hydroperoxide	28	0.9±0.1
Diphenylethyl hydroperoxide	30	0.96±0.11
	107	7.0±0.5
	172	11.2±0.8
	112	7.3±0.5

The occurrence of a strong intramolecular hydrogen bond in α-keto hydroperoxides was pointed out earlier[18].

Di-(1-hydroperoxycyclohexyl) peroxide was investigated by NMR[35]:



The chemical shift of the hydroperoxy-proton does not change in the concentration range 0.2 — 0.01 p.p.m. in carbon tetrachloride solution at 15 — 80°C (9.3 p.p.m.). This value agrees satisfactorily with the δ_a obtained for other hydroperoxides[21,22]. The constancy of the chemical shift of the proton signal of the OOH group in the concentration and temperature range investigated suggests a strong intramolecular hydrogen bond in this compound.

4. INTERMOLECULAR HYDROGEN BONDS IN "HYDROCARBON HYDROPEROXIDE — PROTON ACCEPTOR" COMPLEXES

Like other substances with hydroxy-groups (phenols, alcohols, and acids), hydrocarbon hydroperoxides react with proton acceptors to form hydrogen-bonded association complexes[26]. The formation of the latter may influence the kinetics and mechanisms of reactions involving hydroperoxides which occur in the liquid phase[36]. In this connection the study and experimental determinations of the energy of the hydrogen bonds between hydroperoxides and various proton acceptors is of both theoretical and practical interest.

Systematic studies on the formation of complexes by hydroperoxides with various proton acceptors by spectroscopic methods were begun in 1968. The only earlier study[37] on this problem dealt with the formation of complexes by t-butyl hydroperoxide with different acceptors: styrene, benzene, *o*-dichlorobenzene, and chlorobenzene.

Table 4. The frequencies, integral intensities, and association constants of the hydrogen-bonded complexes of isopropylphenyl hydroperoxide[38].

Acceptor	ν_{OH}, cm^{-1}	$\Delta\nu_{OH}$, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	$10^{-3}A$, litre mole^{-1}cm^{-2}	K, litre mole^{-1}
Carbon tetrachloride	3551	—	30	7.7	—
Chloroform	3530	21	58	9.7	—
o-Dichlorobenzene	3522	29	58	11.7	—
Methylene chloride	3521	30	55	11.8	—
Chlorobenzene	3510	41	54	11.9	—
Iodobenzene	3504	47	72	14.5	—
Benzene and its homologues	3503—3476	48—75	43—55	13.2—14.9	0.17—0.35
Nitrobenzene	3490	61	92	21.9	—
Nitromethane	3485	66	98	22.3	—
Anisole	3435	116	90	25.9	0.46
Acetophenone	3432	119	—	—	2.28
Benzoquinone	3430	121	—	—	1.25
Benzophenone	3425	126	—	—	1.67
Acetonitrile	3417	134	113	30.5	—
t-Butyl peroxide	3400	151	120	35.3	0.65
Acetone	3375	176	—	—	1.92
Cyclohexanone	3365	186	—	—	2.50
Dioxan	3357	194	133	53.2	2.20
Ethyl ether	3335	216	135	60.0	—
Isopropyl ether	3326	225	122	51.2	1.78

Shabalin and Kiva[38] examined the proton-donating capacity of isopropyl hydroperoxide and established that it is intermediate between those of alcohols and phenols. They investigated by infrared spectroscopy the complexes of isopropylphenyl hydroperoxide formed via hydrogen bonding with different proton acceptors. Table 4 lists the frequencies and integral intensities for the infrared spectra of the isopropylphenyl hydroperoxide complexes. Assuming that in all cases the interaction of isopropylphenyl hydroperoxide with a proton acceptor yields a 1 : 1 complex, the authors calculated the association constants K for certain systems (Table 4) using the equation

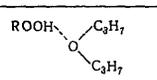
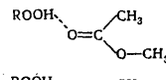
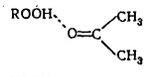
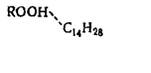
$$K = \frac{1-\frac{D}{D_0}}{\frac{D}{D_0}\left[C_a - C_{hp}\left(1-\frac{D}{D_0}\right)\right]}, \qquad (3)$$

where D_0 and D are the optical densities of the bands due to the free OH groups before and after the addition of the acceptor, C_{hp} is the initial molar concentration of the hydroperoxide, and C_a the molar concentration of the acceptor.

The same workers[39] used infrared spectra to calculate the energies of the hydrogen bonds between isopropylphenyl hydroperoxide and different acceptors. Shabalin et al.[32] also showed that an intermolecular hydrogen bond is formed between the isopropylphenyl hydroperoxide proton and the π electrons in the rings of aromatic solvents. The shift of the band due to bound OH groups is linearly related to the ionisation potential of the aromatic solvent.

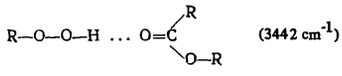
The intermolecular hydrogen bonds have been investigated and the bond energies for the t-butyl hydroperoxide — isopropyl ether and t-butyl hydroperoxide — pentyl acetate systems in carbon tetrachloride have been calculated in the range 20 — 50°C (Table 5)[34].

Table 5. The shifts $\Delta\nu$ of the band due to the C — O — O — H group on formation of the hydrogen bond and the hydrogen bond energy E_H (ROOH = t-butyl hydroperoxide)[34].

Complex	$\Delta\nu$, cm^{-1}	E_H, kcal mole^{-1}
	220	3.7±0.4
	120	3.3±0.3
	172	*
	60	—

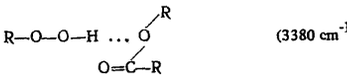
*E_H could not be determined experimentally, since in this system there is a chemical reaction between the donor and the acceptor[40].

On the basis of the infrared spectra, the authors suggest that in the system with the ester, apart from complexes of the type



(3442 cm^{-1})

the complexes



(3380 cm^{-1}),

are formed to a very small extent.

The energy of the hydrogen bond was calculated from the van't Hoff equation:

$$\ln\frac{D_1^H D_2^{bound}}{D_2^H D_1^{bound}} = \frac{E_H(T_2-T_1)}{R\ T_2\ T_1}, \qquad (4)$$

where D^H and D^{bound} are the optical densities of the absorption bands due to the "free" and bound (by hydrogen bonding) C — O — O — H groups at two temperatures.

The possibility of association via hydrogen bonding with aromatic amines was pointed out by Ivanov[41], who established by infrared spectroscopy that in the interaction between aniline and hydroperoxides, which are intermediates in the autoxidation of hydrocarbons, in particular with isopropylphenyl hydroperoxide, these substances undergo association at low temperatures with formation of the following molecular compound:

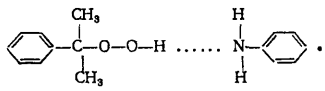


Table 6. Frequencies and half-widths of the infrared absorption band of the OH group and the energies of the intermolecular hydrogen bonds between hydrocarbon hydroperoxides and aromatic solvents.

Solvent	Isopropylphenyl hydroperoxide			t-Butyl hydroperoxide			t-Pentyl hydroperoxide		
	ν, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	ΔE, kcal $mole^{-1}$	ν, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	ΔE, kcal $mole^{-1}$	ν, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	ΔE, kcal $mole^{-1}$
o-Dichlorobenzene	3552	58	0.86	3530	46	0.80	3531	30	0.80
Chlorobenzene	3510	54	1.22	3523	53	1.03	3529	40	0.98
Benzene	3508	40	1.46	3511	46	1.47	3513	45	1.41
Toluene	3500	46	1.50	3508	48	1.53	3510	42	1.51
m-Xylene	3491	48	1.82	3502	49	1.75	3500	46	1.84
Pseudocumene	3484	52	1.98	3496	50	1.95	3497	48	1.95
Durene	3481	55	2.28	—	—	—	—	—	—
Pentamethyl benzene	3476	—	2.26	—	—	—	—	—	—

Recently the authors of the review used NMR and infrared spectroscopy to study the formation of hydrogen bonds in complexes of hydroperoxides with various proton acceptors. Thus more detailed studies were made of the complexes of hydrocarbon hydroperoxides with aromatic solvents[42]. The data in Table 6 shows that the stability of the complexes of hydroperoxides with aromatic solvents increases with the degree of substitution of the protons in the benzene ring by alkyl groups (CH_3). The chemical shifts of the proton involved in hydrogen bonding in the complexes of hydroperoxides with aromatic solvents are satisfactorily correlated with the ionisation potentials of the latter and also with the frequency shifts of the OOH group in the complexes. The higher thermal stability of hydrocarbon hydroperoxides in aromatic solvents (in the presence of an excess of the solvent) compared with aliphatic solvents can be accounted for by the formation of weak intermolecular complexes via hydrogen bonds between the hydroperoxide and the aromatic solvent.

Since the energy of the hydrogen bond in these complexes is lower (Table 6) than in the self-association of hydroperoxides (Table 2), the O — O bond in the hydroperoxide molecule in the complex is weakened less than in the linear hydroperoxide dimer, in consequence of which the hydroperoxide molecule in the complex is more stable than in the linear dimer.

The hypothesis that "aromatic hydrocarbon–hydroperoxide" complexes exist also explains the higher thermal stability of aliphatic-aromatic hydroperoxides compared with aliphatic hydroperoxides dissolved in an inert solvent, for example a saturated aliphatic hydrocarbon.

The formation of complexes of hydrocarbon hydroperoxides with amines has been discussed[43]. The interest in systems comprising hydroperoxides and amines is due to a number of factors. In most cases such systems are used as initiators of polymerisation processes. They are studied in order to find ways of preventing the oxidative degradation of polymers; in many cases amines are employed as inhibitors of the thermal polymerisation of monomers.

NMR data have led to a mechanism of the association of hydrocarbon hydroperoxides with amines using triethylamine as an example. At low triethylamine concentrations, association of the type OH...O (hydroperoxide — hydroperoxide) predominates, at high triethylamine concentrations the N...HO association is dominant, and in the intermediate region the dominant form is

$$\begin{matrix} R_3NH^+ \ldots {}^-OOR_1 \\ \vdots \\ HOOR_1 \end{matrix}.$$

The existence of dimers formed via a polar interaction may be expected in solution, the screening decreasing in the sequence

$$\sigma(OH \ldots O) \simeq \sigma(N \ldots HO) > \sigma(NH^+ \ldots {}^-O).$$

The low thermal stability of hydrocarbon hydroperoxides in the presence of amines and the lower activation energy for their decomposition can be explained by the formation of a strong hydrogen bond between the hydroperoxide and the amine or its salt, which facilitates the cleavage of the hydroperoxide molecule at the weak O — O bond.

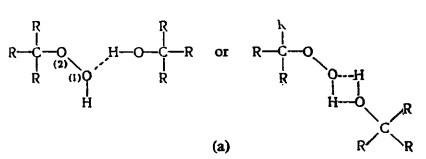
One of the final products of the decomposition of hydrocarbon hydroperoxides is an alcohol. Their interaction with hydroperoxides via hydrogen bonding may influence the rate of decomposition of the hydroperoxide. The formation of complexes by tertiary hydrocarbon hydroperoxides with a number of alcohols has been studied[35] by ^1H NMR. In all the complexes investigated, the energy of the "alcohol — hydroperoxide" hydrogen bond

$$\begin{matrix} R{-}O{-}O{-}H \\ \vdots \\ H{-}O{-}R \end{matrix}$$

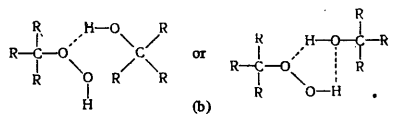
(calculated from the signal of the proton in the alcoholic OH group) is 3.5 — 4.5 kcal $mole^{-1}$ and the energy of the "hydroperoxide — alcohol" bond (ROOH...$\overset{H}{O}$ — R) (calculated from the signal of the proton in the hydroperoxide OOH group) is about 2.5 kcal $mole^{-1}$. Using the thermodynamic data obtained for the association of hydrocarbon hydroperoxides, alcohols, and their complexes, the following sequence may be established in terms of the strength of the hydrogen bond:

$$\left[\begin{matrix}\text{Hydroperoxide}\\ \text{Alcohol}\end{matrix}\right] \simeq \left[\begin{matrix}\text{Hydroperoxide}\\ \text{Hydroperoxide}\end{matrix}\right] < \left[\begin{matrix}\text{Alcohol}\\ \text{Hydroperoxide}\end{matrix}\right] < \left[\begin{matrix}\text{Alcohol}\\ \text{Alcohol}\end{matrix}\right]$$

The dependence of the chemical shifts of the OOH and OH protons in the hydroperoxide — alcohol mixture on the alcohol concentration leads to the possibility of identifying the oxygen atom of the hydroperoxide involved in the association with the alcohol. Generally speaking, one can suppose that the hydrogen bond between the alcohol and the hydroperoxide involves both the first oxygen atom of the hydroperoxide:



and its second oxygen atom:



(b)

The "alcohol — hydroperoxide" hydrogen bond is approximately equally strong for all alcohols. This conclusion is consistent with the finding that

$$\delta^{OH}_{[alcohol]\to 0} \simeq const.$$

It is extremely likely that the hydrogen bond between the alcohol and the hydrogen peroxide involves the first oxygen atom of the latter, since in this case the steric factor is less important. This is confirmed indirectly by the finding that at low hydroperoxide concentrations the "alcohol — hydroperoxide" hydrogen bonds (ROOH...$\overset{H}{O}$—R) depend on the structure of the alcohol (Table 7).

Table 7.

Alcohol	$\Delta\delta_{OOH}$, p.p.m.
C_2H_5OH	2.02
$(CH_3)_2CHOH$	2.00
$(CH_3)_3COH$	1.90
$CH_3(CH_2)_4OH$	1.80
$C_6H_5(CH_3)_2COH$	1.50

$\Delta\delta_{OOH}$ decreases with increasing importance of the steric factor in the alcohol. If the "alcohol — hydroperoxide ("σ") bond involves the second oxygen atom (the position of which is analogous to that of the oxygen atom in the alcohol), a similar relation between $\delta^{OH}_{[alcohol]\to 0}$ and the steric factor of the hydroperoxide would be expected.

The formation of complexes via hydrogen bonds between tertiary hydroperoxides and a ketone and an ether was investigated[43] and the composition of the complexes and their influence on the decomposition of the hydroperoxides were discussed. A study was also made of the complexes of t-butyl hydroperoxide with a number of olefins and dienes formed by hydrogen bonding between the hydroperoxy-proton and the π electrons of the double bond[35]. It has been shown by infrared spectroscopy that the stability of the complexes formed increases with the basicity of the olefins, i.e. with the number of alkyl substituents at the double bond.

The decomposition and dissociation of the complex ROONa.ROOH via the mechanisms[44]

$$\text{(decomposition)} \qquad ROONa \cdot ROOH \rightarrow ROONa + ROH + {}^1/_2O_2, \qquad (5)$$

$$\text{(dissociation)} \qquad \begin{bmatrix} ROONa \\ \vdots \\ HOOR \end{bmatrix} \rightleftarrows ROONa + ROOH, \qquad (6)$$

where R = $(CH_3)_2CC_6H_5$, were investigated by ^1H NMR. In the decomposition of the complex via reaction (5), the ^1H NMR spectrum shows a combined signal due to the hydroperoxide OOH and alcoholic OH groups. The rate constants for the decomposition of the hydroperoxide in the complex and the activation energy for the decomposition process (E = 16.5 ± 1.0 kcal mole^{-1}) were calculated from the variation of the overall chemical shift due to the hydroxyl protons with reaction time and temperature. The reaction was found to be of first order with respect to the hydroperoxide in dilute solutions of the complex.

In dilute solutions the monomer of the complex may dissociate via mechanism (6). The dissociation constant of the complex $K_{30°} = 4.93 \times 10^{-2}$) and its enthalpy of dissociation (ΔH = −12.7 ± 1 kcal mole^{-1}) were calculated from the temperature variation of the chemical shift of the OOH proton in the complex at its different concentrations. The hydrogen bond in the complex of isopropylphenyl hydroperoxide and its sodium salt is much stronger than that formed in the self dissociation of isopropylphenyl hydroperoxide. The low thermal stability of the hydroperoxide in the ROONa.ROOH complex compared with the "pure" hydroperoxide can be accounted for by the effect of the stronger hydrogen bond and hence by the greater weakening of the O — O bond. "Pure" isopropylphenyl hydroperoxide is stable in solution in saturated hydrocarbons up to 130°C, while the hydroperoxide in the ROONa.ROOH complex decomposes at an appreciable rate already at 30°C.

5. THE ROLE OF THE INTERMOLECULAR HYDROGEN BOND IN THE DECOMPOSITION OF HYDROCARBON HYDROPEROXIDES

The study of the kinetics of the liquid-phase oxidation of hydrocarbons showed[45,46] that hydroperoxides, which are formed as intermediates, are cleaved by a unimolecular mechanism under certain conditions and by a bimolecular mechanism under others. The decomposition of the hydroperoxide via two mechanisms has been explained by the formation of a hydrogen bond in hydroperoxide solutions[23]. The addition to the hydrocarbon undergoing oxidation of substances capable of associating with hydroperoxides and thereby rupturing the hydrogen bonds between hydroperoxide molecules leads to a change from bimolecular to unimolecular decomposition[47].

Since hydroperoxides form hydrogen bonds with other oxygen-containing compounds, one may expect that certain oxidation products will influence the decomposition of hydroperoxides and the rate of formation of radicals (by forming various complexes with the hydroperoxide). This hypothesis is confirmed by the finding that the decomposition of hydroperoxides is facilitated in the presence of alcohols[29], organic acids[48], and other compounds capable of forming association complexes with hydroperoxides via intermolecular hydrogen bonds.

A study of the oxidation of decane showed[48] that the linear relation between the rate of branching of the radical chains and the hydroperoxide concentration obtains only in the early stages of the reaction, where the decomposition products still have almost no influence on the reaction. The further non-proportional increase of the concentration of radicals is related to the formation of oxidation products, for example acids. This phenomenon has been studied[49] in the decomposition of n-decyl hydroperoxide in the presence of caproic acid. The authors suggest that the decomposition of the hydroperoxide into radicals takes place via the intermediate formation of the complex

$$ROOH + n\,R'COOH \overset{k}{\rightleftarrows} ROOH \ldots R'COOH \overset{k'}{\rightarrow} RO^{\cdot} + \dot{O}H + R'COOH. \qquad (7)$$

Owing to the formation of hydrogen bonds in this complex, the dissociation of the O — O bond in the hydroperoxide molecule is facilitated, which leads to the formation of radicals. The activation energy for the decomposition of

the hydroperoxide in the ROOH...RCOOH complex is 16.1 kcal mole^{-1}, which is much less than the activation energy for the decomposition of the hydroperoxide in the absence of an acid (23.8 kcal mole^{-1}).

It has also been noted in the literature that the kinetics of the oxidation of hydrocarbons are influenced by solvents in which the oxidation is carried out[50]. The presence in the reaction mass of solvents capable of forming hydrogen bonds with the hydroperoxide leads to a rearrangement of the structure of the association complexes formed with participation of the hydroperoxide which in turn alters the rate of initiation of the oxidation of hydrocarbons. Similar views were also put forward before. For example, it was suggested[51] that pyridine be employed as a kind of catalyst for the oxidation of hydrocarbons, since it forms a hydroperoxide — pyridine complex the decomposition of which at the O — O bond is fairly rapid. The rate constant for the decomposition of t-butyl hydroperoxide into radicals is a factor of 200 higher in the presence of pyridine compared with the pure hydroperoxide. A study of the decomposition of t-butyl hydroperoxide in cyclohexanone showed that the presence of cyclohexanone in the reaction mass greatly accelerates (by a factor of 7 — 10) the decomposition of the hydroperoxide into radicals. The infrared spectra indicate the formation of a complex[52].

The thermodynamic data obtained for complexes of hydrocarbon hydroperoxides with various compounds and the literature data on the activation energies for the decomposition of hydroperoxides have led to a general correlation between the strength of the hydrogen bond in the complex and the activation energy for the hydroperoxide decomposition reaction[53]. With increase of the enthalpy of the hydrogen bond in the hydrocarbon hydroperoxide complexes with various compounds, the activation energy for the decomposition of the hydroperoxide falls. Thus the activation energy for the decomposition of hydroperoxides in aromatic hydrocarbons amounts to 25 — 40 kcal mole^{-1}, while in the presence of amines or in the alkali-catalysed decomposition of hydroperoxides it is 14 — 18 kcal mole^{-1}. A correlation between the chemical shift and the displacement of the stretching vibration frequency of the hydrogen-bonded complexes of hydrocarbon hydroperoxides on the one hand and the activation energy for the decomposition of the hydroperoxides on the other has also been observed.

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